

# Kinetics of Epoxy Resins Formation from Bisphenol-A, Bisphenol-S, and Epichlorohydrin

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## SYNOPSIS

The kinetics of formation of epoxy resins derived from bisphenol-A, bisphenol-S, and epichlorohydrin under stoichiometric conditions was considered. The kinetics of reaction was studied by taking into account the consumption of the added alkali and epoxide value of epoxide oligomers. The obtained results satisfactorily explained that the reactivity of bisphenol-A with epichlorohydrin is higher than that of bisphenol-S, the rate of dehydrochlorination of chlorohydrin ether in the presence of alkali and water is much higher than that of the rate of condensation of phenolic hydroxyl group with epichlorohydrin. The apparent reaction order of phenolic groups with epichlorohydrin and terminal epoxide group in the oligomer are all second order. The rate constants and activation energy were determined. The results are discussed. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

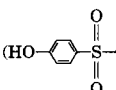
Epoxy resins based on epichlorohydrin (ECH) and bisphenol-S (BPS) have been synthesized.<sup>1-3</sup> This polymer has better heat resistance, gel time, and mechanical properties than that of epoxy resins prepared from epichlorohydrin and bisphenol-A (BPA). The kinetics of formation of epoxy resins based on ECH and BPA have been considered and attempts to develop a mathematical model of the synthesis of epoxy resins have also been made.<sup>4-6</sup> In some cases, a qualitative coincidence of theoretical and experimental data were obtained. However, the process of this reaction is rather complicated, despite having made some progress, the complete kinetic data and the description of the synthesis have been lacking until now. The reaction order is not discussed.

The kinetic analysis of synthesis of epoxy resin improved by bisphenol-S is the purpose of the present investigation. The kinetics of formation of this epoxy resin under stoichiometric conditions was considered. The reactivity of bisphenol-A, bisphenol-S, with ECH and epoxide group (EG) in oligomer, were investigated by taking into account

the consumption of the added alkali and epoxide group.

## EXPERIMENTAL

### Materials

Bisphenol-A and bisphenol-S () were

purified by recrystallization in toluene, melting points are 160°C and 240°C, respectively; epichlorohydrin, dioxane, NaOH, KOH, hydrochloric acid, acetone, and ethyl alcohol were all analytically pure grade. Commercial grade BPA epoxy resin was purified by passage through dissolved benzene and washing with distilled deionized (DDi) water, the water and solvent were then distilled out *in vacuo*. The epoxide value (EV) of this purified epoxy resin is 0.44 mol/100 g.

### Synthesis of BPS Epoxy Resins

Oligomer of epoxy resin based on BPS was synthesized according to Rainer et al.<sup>7</sup> The epoxide value was determined in accordance by the method of Jay.<sup>8</sup> to be 0.42 mol/100 g.

### Determination of Conversion Rate of Reactants

The kinetics of reaction of BPA, BPS with ECH was investigated by taking into account the consumption of added alkali. The initial mole ratio of BPA or BPS, ECH, and NaOH is 1:1:1. To a four-necked flask equipped with a stirrer, a thermometer, and a condenser was added 0.050 mole BPA and 0.050 mole NaOH, 60 mL dioxane, and 30 mL DDI water. The mixture was rapidly stirred and heated to and maintained at reaction temperature ( $\pm 0.2^\circ\text{C}$ ). Then 0.050 mole ECH was added and stirred rapidly. At regular time intervals, .2 mL of reaction mixture was extracted for analysis. The conversion of reactants was determined potentiometrically with 0.1 mol HCl solution. The data were analyzed by computer.

Under the same concentration and initial mole ratio of  $[\text{EG}] : [-\text{phOH}] : [\text{NaOH}] = 1:1:1$ , the reaction rate of terminal epoxide group in oligomer with phenolic group was determined by taking into account the consumption of epoxide group.

### Infrared Analysis

The content of sulfone group in the epoxy resin improved by bisphenol-S was analyzed by the method of Patts.<sup>9</sup> The characteristic absorption peak of sul-

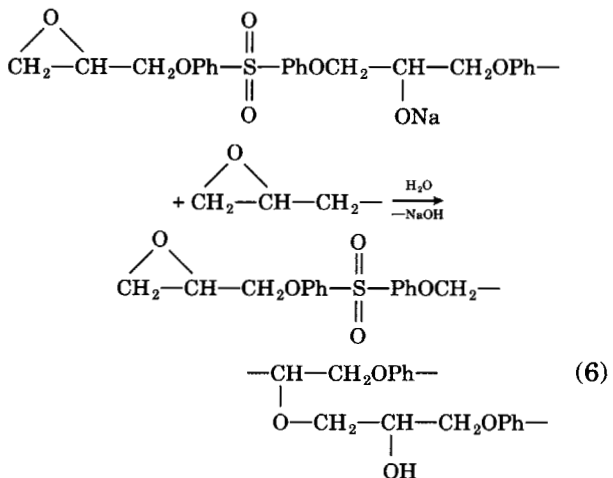
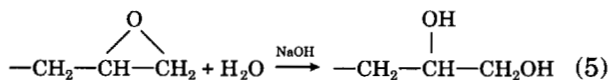
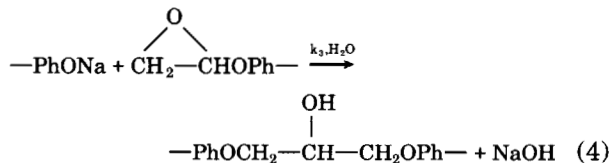
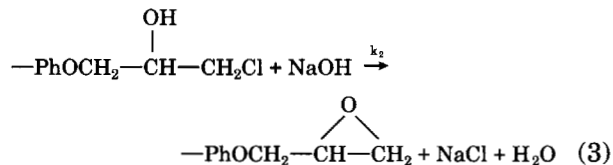
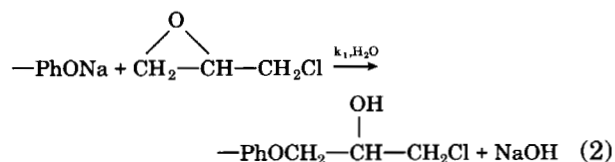
fone group  $\begin{array}{c} \text{O} \\ || \\ -\text{S}- \\ || \\ \text{O} \end{array}$  in BPS is  $1110\text{ cm}^{-1}$ , the ab-

sorption peak of isopropene ( $\text{CH}_3-\text{C}(\text{CH}_3)=\text{CH}_2$ ) in

BPA is  $1180\text{ cm}^{-1}$ .

## RESULTS AND DISCUSSION

The reaction during the interaction of bisphenol with ECH in the presence of alkali in water-organic media follow the main process:



The main postulates on which a kinetic description of the process are based follow:

1. All phenolic groups in monomer and end chains possess the same reactivity as phenol.

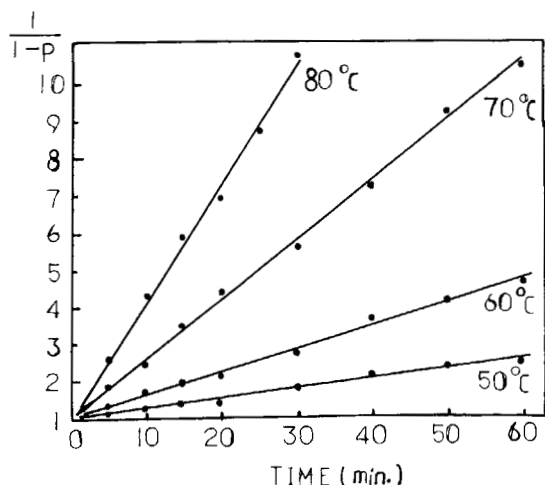


Figure 1 Plot of  $1/(1-P)$  vs. reaction time  $t$  in the reaction of ECH with BPA.

**Table I** Mole Number of EG at Different Ratio of Phenol With ECH at 50°C

No.	Phenol (mol/L)	ECH (mol/L)	Time (min)	EG (mole)
1	1.02	0.44	8	0.20
2	1.02	0.22	8	0.10
3	0.82	4.12	5	0.323
4	0.41	4.12	5	0.161

- The reaction (1) is faster than that of (2) and (4). —  $\text{PhoNa} = \text{NaOH}$ .
- The rate of dehydrochlorination of chlorohydrin ether (CHE) in the presence of alkali in the amount required for complete dehydrochlorination is much higher than the rate of condensation of phenolic hydroxyl groups with ECH and the reaction rate of phenolic hydroxyl groups with terminal epoxide groups (i.e.,  $k_2 \gg k_1, k_3$ ).

Because the concentration of phenolic groups in the first stage of synthesis is higher than that of alkali, all alkali is bound as phenolate ions owing to the high acidity of phenolic hydroxyl groups. Only main reactions (1)–(4) occur in the system; the side reactions of hydrolysis and alcoholysis of ECH and epoxide groups are practically absent and chain branching reactions are also not considered. The kinetic equations have the following form:

$$-\frac{d[\text{ECH}]}{dt} = k_1[\text{NaOH}][\text{ECH}] \quad (7)$$

$$-\frac{d[\text{NaOH}]}{dt} = k_2[\text{NaOH}][\text{CHE}] = k_1[\text{NaOH}][\text{ECH}] \quad (8)$$

$$-\frac{d[\text{EG}]}{dt} = k_3[\text{NaOH}][\text{EG}] - k_1[\text{NaOH}][\text{ECH}] \quad (9)$$

where  $[\text{NaOH}]$ ,  $[\text{ECH}]$ ,  $[\text{CHE}]$ , and  $[\text{EG}]$  are the current concentrations of NaOH, ECH, CHE, and epoxide groups in the oligomers.

### Kinetics of Reaction of ECH with BPA and BPS

According to experimental determination of reaction conversions, the reactions of ECH with BPA were carried out at 50, 60, 70, and 80°C, respectively. If  $P = (E_0 - E)/E_0 = (N_0 - N)/N_0$  (where  $E_0$  and  $N_0$  are the initial concentrations of ECH and NaOH), the relationships of  $1/1-P$  with reaction time  $t$  as shown in Figure 1 is second-order apparent. The order of reactants was determined by changing the molar concentration of reactants<sup>10</sup> and substituting phenol for BPA. The results are listed in Table I. From experiment No. 1 and No. 2, we can see that the reaction occurs first in ECH. Experiment No. 3 and No. 4 prove that the reaction is first-order with respect to phenol.

It is shown that the postulate (3) is correct, that is, reactions (2) and (3) may be considered to proceed in one stage under these conditions. The kinetic equation in the first stage of this reaction is

$$-\frac{d[\text{ECH}]}{dt} = k_{1A}[\text{NaOH}][\text{ECH}]$$

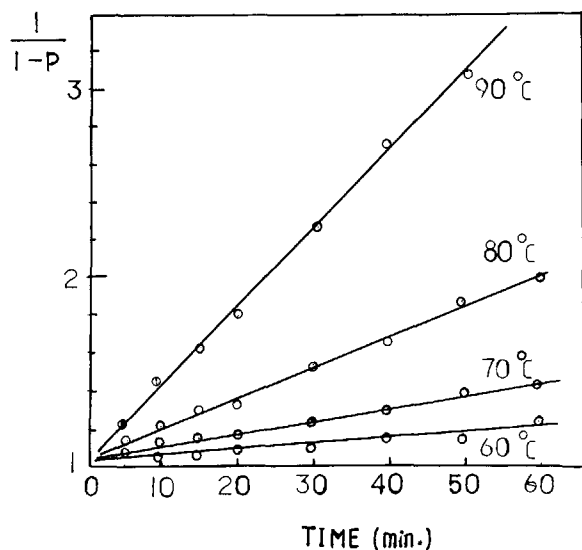
The rate constants  $k_{1A}$  are listed in Table II.

Under the same conditions, the reaction of ECH with BPS was carried out at 60, 70, 80, and 90°C, respectively. The plot of  $1/1-P$  against  $t$  is given in Figure 2. The rate constants  $k_{1s}$  are listed in Table II.

**Table II** Rate Constants  $k_1$ ,  $k_3$  and  $r$  at Various Temperatures

T (°C)		50	60	70	80	90
I	$10^4 \cdot k_{1A}$ (mol L) s	6.2099	12.531	30.493	68.202	
II	$10^4 \cdot k_{3A}$ (mol L) s		1.1860	2.3793	4.8249	
III	$r_A(k_{1A}/k_{3A})$		10.55	12.82	14.14	
IV	$10^4 \cdot k_{1s}$ (mol L) s		0.5816	1.2532	2.8950	6.2513
V	$10^4 \cdot k_{3s}$ (mol L) s		0.3368	0.7122	1.7581	3.5201
VI	$r_s(k_{1s}/k_{3s})$		1.7268	1.7596	1.6467	1.7757

Notes: The linear correlation coefficients of  $k$  are usually between 0.9948–0.9996. The concentrations of reactants are all 0.53 mol/L.



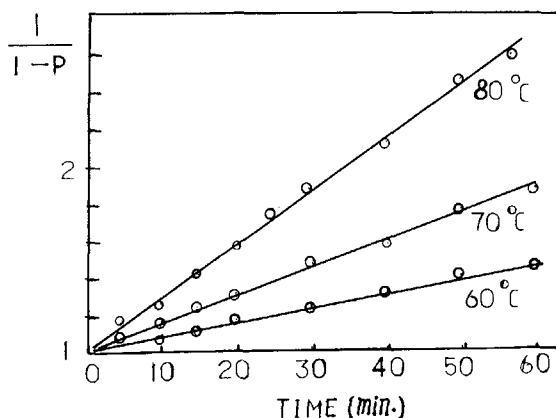
**Figure 2** Plot of  $1/1-P$  vs. reaction time  $t$  in the reaction of ECH with BPS.

According to the Arrhenius equation,  $k = Ae^{-E/RT}$ , plotting  $\ln k_{1A}$  and  $\ln k_{1s}$  against  $1/T$  gave the activation energy  $E_A$  and  $E_S$ , obtained from linear regression analysis as 76.56 and 79.51 kJ/mol, respectively.

### Kinetics of Reaction of Phenol with EG in Oligomer

The reaction of BPA epoxy resin with BPA was carried out in solvents (dioxane-water) and alkali with initial mole ratios of EG:BPA:NaOH = 1:1:1. The kinetic equation of consumption of epoxide group had the following form:

$$-\frac{d[\text{EG}]}{dt} = k_{3A}[\text{EG}][-\text{PhoNa}] \quad (10)$$



**Figure 3** Plot of  $1/1-P$  vs. reaction time  $t$  in the reaction of epoxide group in BPA epoxy resin with BPA.

**Table III** Ratio of Various Rate Constants at 80°C

$\frac{k_{1A}}{k_{1s}}$	$\frac{k_{3A}}{k_{3s}}$	$\frac{k_{3A}}{k_{3A-S}}$	$\frac{k_{3A}}{k_{3S-A}}$	$\frac{k_{3A-S}}{k_{3S}}$
23.5585	2.7444	4.9098	0.9492	0.5590

when the concentrations of reactants were as large as the reaction of ECH with BPA, the results were given in Figure 3. As seen in Figure 3, this reaction is second order. The rate constants  $k_{3A}$  and  $r_A$  ( $r_A = k_{1A}/k_{3A}$ ) are listed in Table II, respectively.

Under the same conditions, we can obtain  $k_{3s}$  and  $r_{3s}$  for the reaction of BPS epoxy resin with BPS (Table II). When the reactions of BPA epoxy oligomer with BPS and BPS epoxy oligomer with BPA were carried out at 80°C, we have the rate constant  $k_{3A-S} = 9.8271 \times 10^{-5}$  and  $k_{3s-A} = 5.0829 \times 10^{-4}$ .

A comparison of reactivity between BPA with BPS and the epoxide group in BPA epoxy resin with the epoxide group in BPS epoxy resin at 80°C is made in Table III.

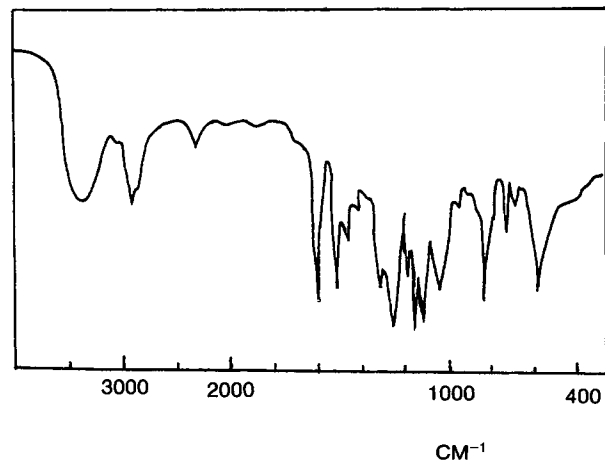
As is seen from Table III, the reactivity of BPA is higher than that of BPS, but the reactivity of the epoxide group of BPS epoxy resins is higher than that of epoxide group of BPA epoxy resins. The differences of reactivity are brought about by the following factors: (1) The acidity of phenolic group of BPS is higher than that of BPA and the nucleophilic reactivity of phenolic anion of BPA is higher than that of BPS. (2) The electrophilic reactivity of the epoxide group of BPS epoxy resin is higher than that of BPA epoxy resin and is due to the greater electron-attraction of sulfonic group at para position, which decreases the resonance electron availability on oxygen atoms and facilitates the formation of protons. Hence, BPS is more acidic than the phenols and BPA.

In accordance with the results, the BPA was consumed more rapidly than BPS in the first stage of synthesis, that is to say, it contained more BPA in

**Table IV** Content (%) of BPS in the Product at Different Reaction Times and Temperatures

$t$ (min)	30	45	60	80
55°C	12.84	19.29	27.12	34.52
80°C	18.18	26.04	37.14	44.63

Note: [ECH] : [BPA] : [BPS] : [NaOH] = 1.0 : 0.5 : 0.5 : 1.1; Dioxane and water were used as solvents.



**Figure 4** Infrared spectrum of epoxy resin improved by bisphenol-S.

the product at the early stage. Infrared analysis of BPS in the product at different reaction times is shown in Table IV, and the theory of this reaction correct. The infrared spectrum of this product is shown in Figure 4.

## CONCLUSIONS

The reactions of BPA and BPS with epichlorohydrin in the presence of alkali in water-organic medium are second order apparent. The rate of dehydrochlorination of chlorohydrin ether in the presence of alkali-water is very fast. Reactions (2) and (3)

may be considered to proceed in one stage under these conditions.

The reaction of epoxide group in molecular end chains with phenol in alkali medium is second order.

The reactivity of bisphenol-A with epichlorohydrin is higher than that of bisphenol-S. Hence, the content of BPA in the product at early stage of the reaction is higher than that of BPS.

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